Photon echoes stimulated from an accumulated grating

Hesselink, Wim H.; Wiersma, Douwe A.

Published in:
The Journal of Chemical Physics

DOI:
10.1063/1.442647

Publication date:
1981

Photon echoes stimulated from an accumulated grating: Theory of generation and detection

Wim H. Hesselink and Douwe A. Wiersma

Picosecond Laser and Spectroscopy Laboratory of the Department of Physical Chemistry, The University of Groningen, Nijenborgh 16, 9747 AG Groningen, The Netherlands
(Received 16 October 1980; accepted 16 June 1981)

We present a theoretical description of the generation and detection of photon echoes, stimulated from an accumulated frequency grating in the inhomogeneous distribution. We show that detection of the echoes takes place via interference in the sample between a properly phased and directed probe pulse and the echo polarization. In this description the echo phenomenon emerges as an induced transparency of the sample rather than a burst of coherent radiation. By solving simultaneously the optical Bloch and Maxwell equations, an expression is obtained which correlates quantitatively the echo intensity to the decay parameters, pulse intensity, and the transition moment. As an application of the theory we present results on the intersystem crossing of pentacene in naphthalene at 1.5 K.

I. INTRODUCTION

Recently, we reported the observation of picosecond photon echoes stimulated from an accumulating grating.[1] This grating can be built up by a train of twin excitation pulses, provided that a bottleneck is present in the relaxation path of the excited state. Due to the high time resolution and relative simplicity of the setup, this photon echo method proved very convenient for measurement of picosecond dephasing[2] and relaxation processes.[2,3] We showed previously that the echo under certain phase-match conditions can easily be detected because interference occurs between the echo and an excitation pulse. However, this description failed to describe quantitatively the observed transients. In particular, the fact that the coherent and background signal (due to saturation) were of comparable intensity would not be expected. In general, the echo intensity is only a few percent of the excitation pulse intensity. This is due to the limited interference efficiency of the phased optical oscillators.[4]

In this paper we give a detailed description of the accumulated echo formation and detection. It is shown by considering simultaneously the Maxwell and Bloch equations, in a fashion analogous to the description of self-induced transparency,[5] that the above mentioned interference between probe pulse and echo polarization takes place *in the sample*. Therefore, this echo phenomenon is more properly described as a transparency effect than as a burst of coherent radiation.

Using the results of this theory, we can predict quantitatively the expected grating intensity, once the decay parameters are known. This is important since it is now possible to predict quite accurately the applicability of the accumulated echo technique to a specific molecular or atomic system. It is of course also possible to obtain from the measured echo intensity information about the decay parameters. Using this approach, we studied the intersystem crossing of pentacene in naphthalene. The results are also presented in this paper.

II. THEORY

A. Echo detection

Before discussing the echo detection in detail, we will briefly review the accumulated echo experiment, which is shown schematically in Fig. 1. We apply a train of twin (picosecond) excitation pulses with a time t_{12} between the pulses and T between the pairs. The intense pump beam (pulses 1 and 3) and the weak probe beam (pulses 2 and 4) are focused at the same spot in the sample. The intensity of the probe beam is phase sensitivity detected at the modulation frequency of the pump beam. Therefore, the change in probe beam intensity, induced by the pump beam, is detected just as in an absorption recovery experiment. The molecular system is represented by a three level scheme, shown in Fig. 2. Levels $|1\rangle$ and $|2\rangle$ are coupled by the radiation field, and level $|3\rangle$ can act as a bottleneck in the relaxation path of $|2\rangle$. We will describe the system in terms of the density matrix in the rotating frame, (designated by $\tilde{\rho}$). Note that we do not include the factor $\exp i(\mathbf{k}\cdot\mathbf{r}+\phi)$ in the transformation to the rotating frame in order to consider the effects of direction and phase of the radiation field explicitly [cf. Eq. (3)]. The off-diagonal elements between level $|3\rangle$ and the levels $|1\rangle$ and $|2\rangle$ will be neglected since no coherence is induced on these transitions.

The pulses will be represented by square waves of duration τ_p and area $\theta=\chi\tau_p$, where χ is the Rabi frequency. The theory presented in this paper applies to the case where low intensity pulses are used, which are short compared to the inverse inhomogeneous width (sharp line absorber). This leads to the following assumptions: $\theta\ll 1$ and $\Delta\tau_p\ll 1$, where Δ is the detuning in the inhomogeneous width. Furthermore, relaxation during the pulse is neglected: $\tau_p\ll T_2$.

The effect of a pulse on the system can now be found by the action of the operator $A(\theta)$ in Liouville space on the density matrix. An explicit expression for $A(\theta)$ is given in Ref. 3. However, in deriving this expression resonant excitation is assumed (corresponding to χ

 0021-9606/81/214192-06$01.00

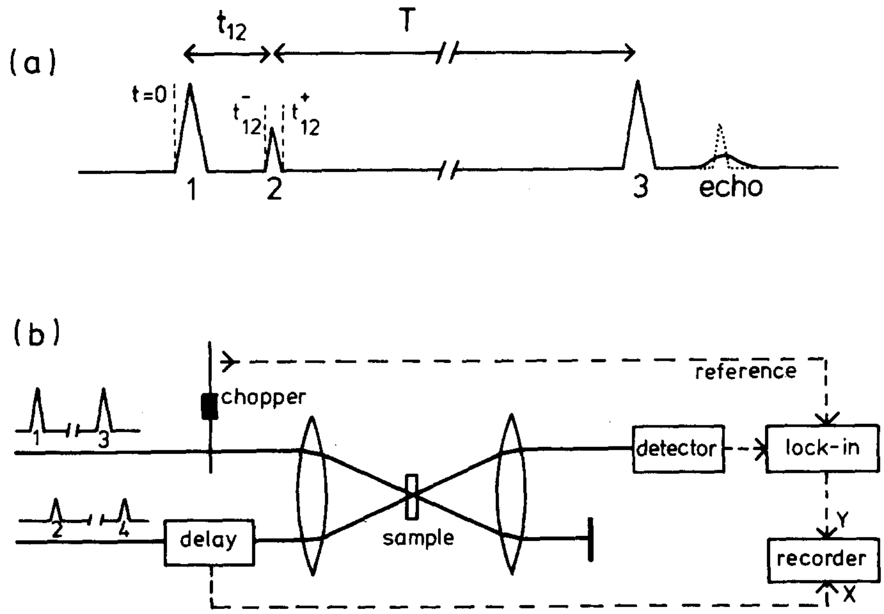

FIG. 1. Schematics of the experimental setup for the detection of photon echoes simulated from an accumulated grating. Note that the echo in time overlaps with a probe pulse.

$\gg \Delta$). This assumption does not hold for a description of the accumulated echo since we deal here with low intensity pulses. Therefore, a slightly different approach is taken, starting from the general solution of the Bloch equation. Since the radiation field only couples states $|1\rangle$ and $|2\rangle$, we have essentially a two level system during excitation and we can apply the familiar equations of motion for the Bloch vector

$$\dot{u} = -\Delta v + w\chi \sin\alpha_i - (u/T_2)\ , \tag{1a}$$

$$\dot{v} = \Delta u + w\chi \cos\alpha_i - (v/T_2)\ , \tag{1b}$$

$$\dot{w} = -\chi v \cos\alpha_i - u\chi \sin\alpha_i\ , \tag{1c}$$

where

$$\alpha_i = \mathbf{k}_i \cdot \mathbf{r} - \phi_i$$

and

$$\begin{aligned} u &= \tilde{\rho}_{12} + \tilde{\rho}_{21}\ , \\ v &= i(\tilde{\rho}_{21} - \tilde{\rho}_{12})\ , \\ w &= \tilde{\rho}_{22} - \tilde{\rho}_{11}\ . \end{aligned} \tag{2}$$

Note that after a series of pulses level $|3\rangle$ becomes populated, as discussed below. This means that the Bloch vector in Eq. (2) is not normalized, when a time scale long compared to k_{23}^{-1} is considered. The general solution of Eq. (1)[6] can be simplified by applying the above mentioned assumptions ($\chi\tau_p$, $\Delta\tau_p \ll 1$, $T_2 \gg \tau_p$), leading to the following result for $A(\theta)$:

$$\begin{pmatrix} u(\tau_p) \\ v(\tau_p) \\ w(\tau_p) \end{pmatrix} = \begin{pmatrix} 1 - \frac{1}{2}(\Delta\tau_p)^2 - \frac{1}{2}\theta^2 \sin^2\alpha_i & -\Delta\tau_p - \frac{1}{4}\theta^2 \sin 2\alpha_i & \theta \sin\alpha_i \\ \Delta\tau_p - \frac{1}{4}\theta^2 \sin 2\alpha_i & 1 - \frac{1}{2}(\Delta\tau_p)^2 - \frac{1}{2}\theta^2 \cos\alpha_i^2 & \theta\cos\alpha_i \\ -\theta\sin\alpha_i & -\theta\cos\alpha_i & 1 - \frac{1}{2}\theta^2 \end{pmatrix} \begin{pmatrix} u(0) \\ v(0) \\ w(0) \end{pmatrix}\ . \tag{3}$$

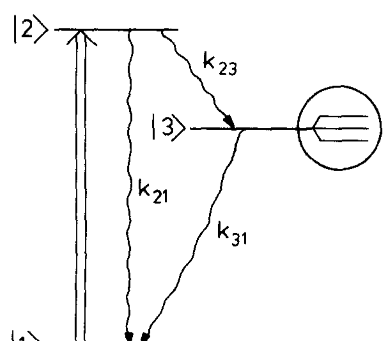

FIG. 2. Level scheme for the electronic origin of a typical organic molecule. $|1\rangle$ is the ground state, $|2\rangle$ the excited singlet state, and $|3\rangle$ the triplet state. The part within the circle has a greatly magnified ($\approx 10^4$) energy scale.

Note that Eq. (3) does not hold for regions around $\alpha = n \cdot (\pi/2)(n = 0, 1, 2, \ldots)$. However, these regions are small when $\Delta\tau_p \ll 1$ as assumed above. This simplification is necessary since otherwise a closed solution, as given in Sec. II B, cannot be found for the behavior of the system when a pulse train is applied. If necessary, the effect of the radiation field on the individual elements of the density matrix can be found by combination of Eqs. (2) and (3).

In between the pulses the evolution of the system is governed by the detuning in the inhomogeneous width (Δ) and the decay parameters. Solving the Bloch equations for the off-diagonal elements and the kinetic equations for the diagonal elements results in the following expression for the operator $B(t)$, describing the time evolution of the system:

$$\rho(t)=B(t)\rho(0)=\begin{bmatrix} 1 & 0 & 0 & 1-\beta e^{-k_{31}t}+(\beta-1)e^{-t/T_1} & 1-e^{-k_{31}t} \\ 0 & e^{[i\Delta-(1/T_2)t]} & 0 & 0 & 0 \\ 0 & 0 & e^{[-i\Delta-(1/T_2)t]} & 0 & 0 \\ 0 & 0 & 0 & e^{-t/T_1} & 0 \\ 0 & 0 & 0 & \beta e^{-k_{31}t}-\beta e^{-t/T_1} & e^{-k_{31}t} \end{bmatrix}\begin{pmatrix}\rho_{11}(0)\\ \rho_{12}(0)\\ \rho_{21}(0)\\ \rho_{22}(0)\\ \rho_{33}(0)\end{pmatrix}, \tag{4}$$

where $\beta = k_{23}/(k_{21}+k_{23}-k_{31})$. T_1 is the population relaxation time of level $|2\rangle$, equal to $(k_{21}+k_{23})^{-1}$, and T_2 is the phase relaxation time (including population relaxation) of the $1\rightarrow 2$ transition. The expressions for $B(t)$ given in Ref. 3 can be obtained from Eq. (1) in the appropriate limits. With the operators given in Eqs. (3) and (4) the effect of an arbitrary pulse cycle can be described.

We now turn to the specific pulse sequence of Fig. 1. To simplify the problem, we assume population relaxation to be negligible during t_{12}: k_{21}, k_{23}, $k_{31} \ll t_{12}^{-1}$. This implies that we have simply a two-level system during t_{12}, in which only dephasing occurs, that we can describe in terms of the Bloch equations. Between the pulse pairs we include population relaxation and consider a three-level system using Eq. (4). Assuming the system to be initially in the ground state ($\rho_{11}=1$, all other elements zero), we find, after two pulses (at time t_{12}^{+}) by repetitive application of Eqs. (3) and (4), for the inversion parameter

$$w(t_{12}^{+})=(1-p)-1\ , \tag{5}$$

where the excitation parameter p is defined by

$$p=\left(1-\frac{\theta_1^2}{2}\right)\left(1-\frac{\theta_2^2}{2}\right)-\theta_1\,\theta_2 \times\exp(-t_{12}/T_2)\cos(\Delta t_{12}-\mathbf{k}_{12}\cdot\mathbf{r}+\phi_{12})\ . \tag{6}$$

The subscripts 1 and 2 refer to the pump and probe pulse, respectively, and $\mathbf{k}_{12}=\mathbf{k}_1-\mathbf{k}_2$ and $\phi_{12}=\phi_1-\phi_2$. The parameter p contains the grating term ($\cos\Delta t_{12}$) which is responsible for the echo as was shown in our previous letter.[1] We will now discuss the echo detection. In the next section we show that, once equilibrium is reached by exciting the sample with the pulse train during a time long compared to k_{31}^{-1}, the inversion parameter before the arrival of a pulse pair (at $t=0$) can be described by

$$w(0)=(1-p)\,\gamma-1\ . \tag{7}$$

Equation (7) is equal to Eq. (5) apart from an enhancement factor γ, evaluated in the following section. Since we assume $T\gg T_2$, $u(0)$ and $v(0)$ are equal to zero.

After a pump pulse and decay during t_{12} we find, shortly before the arrival of the probe pulse ($t=t_{12}^{-}$), from Eqs. (3) and (4),

$$u(t_{12}^{-})=-w(0)\,\theta_1\,e^{-t_{12}/T_2}\sin(\Delta t_{12}-\mathbf{k}_1\cdot\mathbf{r}+\phi_1)\ , \tag{8a}$$

$$v(t_{12}^{-})=w(0)\,\theta_1\,e^{-t_{12}/T_2}\cos(\Delta t_{12}-\mathbf{k}_1\cdot\mathbf{r}+\phi_1)\ , \tag{8b}$$

$$w(t_{12}^{-})=w(0)\left(1-\frac{\theta_1^2}{2}\right)\ . \tag{8c}$$

We now consider the transmission of the probe pulse through the sample which is polarized according to Eqs. (7) and (8). The coupling between the Maxwell and Bloch equations is done in a way analogous to the description of self-induced transparency by McCall and Hahn.[5]

We start with the electromagnetic wave equation

$$\frac{\partial^2 E}{\partial z^2}=\frac{\eta^2}{c^2}\,\frac{\partial^2 E}{\partial t^2}+\frac{1}{\epsilon_0 c^2}\,\frac{\partial^2 P}{\partial t^2}\ , \tag{9}$$

where η is the index of refraction, c is the velocity of light, and ϵ_0 is the electric permittivity of free space. For simplicity, we only consider one direction, which is the direction of propagation of the probe pulse. We describe the optical field by a real plane polarized wave

$$E(z,\ t)=E_0(z,\ t)\cos(\omega t-k_2 z+\phi_2)\ , \tag{10}$$

where E_0 is the slowly varying pulse envelope. The Z axis is the direction of propagation of the probe beam. The polarization in the medium is given by

$$P=N\int_{-\infty}^{+\infty} g(\Delta)\,\mathrm{Tr}(\mu\rho)\,d\Delta\ , \tag{11}$$

where N is the density of absorbing molecules and $g(\Delta)$ is the normalized inhomogeneous distribution function. For the expectation value of the dipole operator we find

$$\begin{aligned}\mathrm{Tr}(\mu\rho)&=\mu_{12}(\rho_{12}+\rho_{21})\\ &=\mu_{12}[u'\cos(\omega t-kz)-v'\sin(\omega t-kz)]\ .\end{aligned} \tag{12}$$

Here $(u',\ v',\ w')$ is the Bloch vector obtained by including the phase factor $\exp i(\mathbf{k}_2\cdot\mathbf{r}-\phi_2)$ in the transformation to the rotating frame. This factor obeys the familiar equations of motion without the factor α_i [$\alpha=0$ in Eq. (1)]. When we substitute Eqs. (10)–(12) in Eq. (9) and neglect the second derivatives of E_0, and terms $\sim\dot{u}/\Delta$, we arrive at an expression for the pulse envelope

$$\frac{\partial E_0}{\partial z}=-\frac{\eta}{c}\,\frac{\partial E_0}{\partial t}+\frac{\omega N\mu_{12}}{2\epsilon_0\,\eta c}\int_{-\infty}^{+\infty} g(\Delta)\,v'(\Delta,\ \mathbf{r},\ t)\,d\Delta\ . \tag{13}$$

As we are interested in the total pulse intensity, we integrate Eq. (13) over the pulse duration. The pulse area is defined as

$$\theta(z)=\frac{\mu_{12}}{\hbar}\int_{\tau_p}E_0(z,\,t)\,dt\,. \tag{14}$$

We then find

$$\frac{\partial\theta}{\partial z}=\frac{\omega N\mu_{12}^2}{2\hbar\epsilon_0\eta c}\int_{\tau_p}\int_{-\infty}^{+\infty}g(\Delta)\,v'(\Delta,\,\mathbf{r},\,t)\,dt\,d\Delta\,. \tag{15}$$

We now have to insert an expression for v from the Bloch equations in Eq. (13). Note that the treatment of McCall and Hahn[5] does not apply to our problem as we consider here a sharp line absorber ($\tau_p \ll 1/\Delta$). We obtain from Eq. (1c) the equations of motion for $\dot{w}'$ [Eq. (1c) with $\alpha=0$]:

$$v'=-\frac{\dot{w}'}{\chi}=-\frac{\dot{w}}{\chi}\,. \tag{16}$$

If we assume the pulse profile in time to be a square wave, the integration over τ_p in Eq. (15) becomes trivial since the Rabi frequency χ is now constant:

$$\int_{\tau_p}v'dt=-\frac{1}{\chi_2}\left[w(t_{12}^+)-w(t_{12}^-)\right]=\frac{1}{\chi_2}\left[\frac{\theta_2^2}{2}\left(1-\frac{\theta_1^2}{2}\right)\right.$$
$$\left. w(0)+\theta_1\theta_2\,w(0)\,e^{-t_{12}/T_2}\cos(\Delta t_{12}-\mathbf{k}_{12}\cdot\mathbf{r}+\phi_{12})\right]\,, \tag{17}$$

where $w(t_{12}^+)$ is obtained by applying the matrix given in Eq. (3) on Eq. (8), and $w(t_{12}^-)$ is given in Eq. (8c). We now insert Eqs. (6), (7), and (17) in Eq. (15) and perform the integration over the inhomogeneous distribution. We assume $t_{12}\gg 1/\delta\omega_{\text{inh}}$, where $\delta\omega_{\text{inh}}$ is the width of the inhomogeneous distribution $g(\Delta)$. This implies neglect of interaction of the probe pulse with the free induction decay induced by the pump pulse.

The two terms in Eq. (17) have a distinct physical meaning: The first term corresponds to the absorption, saturated by accumulating population in state $|3\rangle$ and by the excitation pulse immediately preceeding the probe pulse. Only the first term in the excitation parameter (6) contributes, since the second term averages to zero upon integration over Δ. Therefore, we find

$$\int_{-\infty}^{+\infty}g(\Delta)\,w(0)\,d\Delta=\left[1-\left(1-\frac{\theta_1^2}{2}\right)\left(1-\frac{\theta_2^2}{2}\right)\right]\gamma-1\,. \tag{18}$$

[The second term in Eq. (17) corresponds to the interaction of the probe pulse with the echo polarization. The only nonzero part in the integration is the one containing the grating term of Eq. (6) since all other terms contain oscillating factors and average to zero:

$$\int_{-\infty}^{+\infty}g(\Delta)\,w(0)\cos(\Delta t_{12}-\mathbf{k}_{12}\cdot\mathbf{r}+\phi_{12})\,d\Delta$$
$$=\gamma\theta_1\,\theta_2\,e^{-2t_{12}/T_2}\int_{\infty}^{\infty}g(\Delta)\cos^2(\Delta t_{12}-\mathbf{k}_{12}\cdot\mathbf{r}+\phi_{12})\,d\Delta\,. \tag{19}$$

This equation describes the crucial point of the interaction between the echo polarization and probe pulse. By considering the integration in the right-hand side of Eq. (19), it is obvious that the wave vector and phase dependence of the echo term is *completely eliminated*, for the integral simply yields 0.5. This contrasts with the familiar description of the echo formation in which the constructive interference of the phased dipoles leads to a directional radiation pattern. In that case, due to geometrical factors,[4] the intensity in the major radiation lobe is limited to a few percent. This reduction is overcome in our method by interference in the sample with a properly phased and directed probe pulse.

By combining Eqs. (15) and (17)–(19), we obtain

$$\frac{\partial\theta_2}{\partial z}=\alpha\,\frac{\tau_p}{2\pi g(0)}\left[\left(1-\frac{\theta_1^2}{2}+2e^{-2t_{12}/T_2}\right)\frac{\theta_1^2\gamma}{4}\right.$$
$$\left.-\frac{1}{2}\left(1-\frac{\theta_1^2}{2}\right)\right]\theta_2\,, \tag{20}$$

where we assumed $\theta_2(\text{probe})\ll\theta_1(\text{pump})\ll 1$ and used the relation $\theta_2=\chi_2\tau_p$ for the area of a square wave. The absorption coefficient is defined as[7]

$$\alpha=\frac{\pi\omega N\mu^2 g(0)}{cn\hbar\epsilon_0}\,. \tag{21}$$

Equation (20) is simply Beer's law for absorption, be it with a rather complex absorption coefficient. By integrating Eq. (20) over z, we obtain the final result for the probe pulse intensity for a square wave proportional to the area squared:

$$I_2(l)=I_2(0)$$
$$\times\exp\left\{-\alpha_{\text{eff}}\left[1-\frac{\theta_1^2}{2}-\left(1-\frac{\theta_1^2}{2}+2\,e^{-2t_{12}/T_2}\right)\frac{\theta_1^2\gamma}{2}\right]l\right\}, \tag{22}$$

where l is the sample length and the effective absorption coefficient is defined as

$$\alpha_{\text{eff}}=\alpha\,\frac{\tau_p}{2\pi g(0)}\,. \tag{23}$$

[In the absence of the first excitation pulse ($\theta_1=0$), Eq. (22) simply gives the absorption law for the probe pulse. The reduction of the absorption coefficient [Eq. (23)] is due to the fact that we assumed the pulse width to be much shorter than the inverse inhomogeneous width. Therefore, the pulse has appreciable spectral components outside the absorption line.[8]

The additional θ_1 dependent term in Eq. (22) has a positive sign and therefore corresponds to a *transparency* induced in the sample by the first pulse. The two components of this term have a distinct physical meaning as already mentioned above: an incoherent part (the ordinary saturation) and a coherent part (the echo) which contains the information about the phase loss during t_{12}. The interesting point is now that both terms depend in the same way on the intensity of the first pulse and on the enhancement factor γ. This means, from an experimental point of view, that the echo is just as easily detectable as the saturation.

The $1-(\theta_1^2/2)$ terms in Eq. (22) correspond to saturation induced by the excitation pulse, preceding the probe pulse. These terms can be taken equal to unity when $\gamma\gg 1$ (the accumulation effect much larger than the single pulse effect).

The nice result of the description given in this section is that Eq. (22) correlates, quite unexpectedly, the observed increase in probe pulse transmission directly and quantitatively to the echo amplitude.

We have shown previously [Fig. 2(c) of Ref. 1] that both components of the induced transparency are indeed observed experimentally. However, instead of the expected 1 : 2 ratio ($\gamma \gg 1$, $\theta_1 \ll 1$) between background and echo intensity, we observe only a ratio of approximately 1 : 1.3. This discrepancy can be due to several factors. First, our pulses are not short enough to entirely justify the assumption of negligible inhomogeneous dephasing during the pulse. This means that the coherent excitation of the wings of the absorption line is not as efficient as that of the center of the line. Therefore, the grating can be slightly disturbed in the wings. In the second place, an often present frequency chirp[9] in the pulse can disturb the grating, while the incoherent saturation is not affected.

B. Dependence of the echo intensity on the decay parameters

In this section we will derive expressions for the grating intensity in a two- and three-level system. We start with a population distribution given by $\rho_{11}(0)$, $\rho_{22}(0)$, and $\rho_{33}(0)$ and assume the off-diagonal elements to be zero. After two excitation pulses we find for the diagonal elements

$$\rho_{11}(t_{12}^{+}) = \tfrac{1}{2}(1+p)\rho_{11}(0) + \tfrac{1}{2}(1-p)\rho_{22}(0) , \tag{24a}$$

$$\rho_{22}(t_{12}^{+}) = \tfrac{1}{2}(1-p)\rho_{11}(0) + \tfrac{1}{2}(1+p)\rho_{22}(0) , \tag{24b}$$

$$\rho_{33}(t_{12}^{+}) = \rho_{33}(0) , \tag{24c}$$

where the excitation prameter p is defined by Eq. (6) and population relaxation during t_{12} is neglected. Note that these equations simplify to Eq. (5) when taking $\rho_{11}(0) = 1$ and $\rho_{22}(0) = \rho_{33}(0) = 0$. We assume now that $T_2 \ll T$, which means that the off-diagonal elements of the density matrix have vanished when the next pair of pulses arrives at time T. This assumption is quite reasonable as the accumulated echo technique is especially suited for studying ultrafast phase relaxation processes. Furthermore, we are in this section primarily interested in the maximum echo intensity at small delay times t_{12}.

The decay during time T can be described by multiplication of ρ by the decay matrix B, defined in Eq. (4), where only those elements of B have to be considered that act upon the diagonal elements of ρ:

$$\rho(T) = B(T)\rho(t_{12}^{+}) . \tag{25}$$

Once we have reached a steady state after applying the pulse train during a time long compared to the bottleneck lifetime (k_{31}^{-1}), the equilibrium condition applies:

$$\rho(T) = \rho(0) , \tag{26}$$

stating that the excitation of the system with one pair of pulses should exactly compensate the losses, due to relaxation during a time T. By substituting Eqs. (26) and (4) in Eq. (25) and taking the normalization ($\sum_i \rho_{ii} = 1$) into account, a solution for the diagonal elements of ρ can be found:

$$\rho_{11}(0) = 1 - (1-p)\,\frac{e^{-T/T_1}(1-\beta-e^{-k_{31}T}) + \beta\, e^{-k_{31}T}}{2D} , \tag{27a}$$

$$\rho_{22}(0) = (1-p)\,\frac{e^{-T/T_1}(1-e^{-k_{31}T})}{2D} , \tag{27b}$$

$$\rho_{33}(0) = (1-p)\,\frac{\beta(e^{-k_{31}T} - e^{-T/T_1})}{2D} , \tag{27c}$$

where the denominator is given by

$$D = 1 - e^{-k_{31}T}\left[1 - \frac{\beta}{2}(1-p)\right] - e^{-T/T_1}\left[p(1-e^{-k_{31}T}) + \frac{\beta}{2}(1-p)\right] . \tag{28}$$

These expressions can be simplified by making the following approximations:

(1) small excitation pulses: $p \approx 1$;

(2) a "true" bottleneck: $k_{31}^{-1} \gg T$, which implies $e^{-k_{31}T} \approx 1$;

(3) no additional bottleneck in state $|2\rangle$: $k_{31}^{-1} \gg (k_{21} + k_{23})^{-1}$ and therefore

$0 < \beta < 1$.

With these three approximations Eq. (28) reduces to

$$D \approx 1 - e^{-k_{31}T} . \tag{29}$$

The important point is that D is independent of the excitation parameter p. Therefore, we can now derive the expression for the steady state inversion parameter, which we already used in the previous section [Eq. (7)], by combining Eqs. (27) and (29):

$$w(0) = (1-p)\gamma - 1 , \tag{30}$$

with the enhancement factor

$$\gamma = \frac{e^{-T/T_1}[2(1-e^{-k_{31}T}) - \beta] + \beta\, e^{-k_{31}T}}{2(1-e^{-k_{31}T})} . \tag{31}$$

So far we have discussed the accumulation effect in a three-level system, but the effect can of course also appear in a two-level system provided $T_1 \gg T$. In this situation, which corresponds to $k_{23} = 0$ and therefore $\beta = 0$, we can calculate the factor γ directly from Eqs. (27) and (28):

$$\gamma = \frac{e^{-T/T_1}}{1 - p e^{-T/T_1}} \approx \frac{e^{-T/T_1}}{1 - e^{-T/T_1}} , \tag{32}$$

where we used again the approximation of low excitation intensity ($p \approx 1$).

When these expressions for γ are inserted in Eq. (22), an expression for the echo intensity is obtained which depends only on the decay parameters, the intensity and duration of the pulses, and the absorption of the transition.

III. THE INTERSYSTEM CROSSING OF PENTACENE

The theory given in the preceding sections enables us to predict quantitatively the echo intensity or alternatively to obtain information about the decay channels. In our experiments we use square wave modulation of the pump beam, which means that we measure the difference between the probe beam intensity with the pump on (I_{on}) and off (I_{off}). It is easy to calculate from Eq. (22) that the relative probe beam intensity is given by

$$S(t_{12}) = \frac{I_{on} - I_{off}}{I_{off}}$$
$$\approx \alpha_{eff} \left[\frac{\theta_1^2}{2} (\gamma + 1) + \theta_1^2 \gamma e^{-2t_{12}/T_2} \right] l , \qquad (33)$$

under the assumptions $S(t_{12})$, $\theta_1 \ll 1$.

We apply the theory now to a study of the intersystem crossing (ISC) of pentacene in naphthalene at low temperature. A typical accumulated echo experiment on the electronic origin was performed under the following conditions: average power density in the pump beam at the sample of 1.5 W/cm^2, $\tau_p = 24$ ps, $T = 12.2$ ns, $\alpha_{eff} l = 0.87$, and index of refraction of the sample of 1.7.

With a transition dipole moment of 0.7 D,[11] we arrive at $\theta_1 = 0.045$ rad assuming a Gaussian pulse shape. From the observed $S(\infty) = 0.11$ we calculate from Eq. (33) that $\gamma = 124$, indicating two orders of magnitude enhancement of the accumulated signal over the single pulse signal! This value for γ can be used to calculate the ISC rate from Eq. (31), since all other parameters are known. Previously, we reported the observation of two components in the decay of the grating, with relaxation times of 15 μs and 2.3 ms.[1] Obviously, these two components correspond to the decay of two of the triplet spin sublevels. From the integrated intensity of the two components we calculate a ratio of steady state population of 1 : 69, indicating that only the long living spin sublevel (Z) needs to be considered here.

With $T_1 = 19.5$ ns and $k_{31} = 435$ s^{-1} we calculate from Eq. (31) for the ISC yield to the Z spin sublevel $\beta = 2.8 \times 10^{-3}$.

Recently, van Strien and Schmidt[10] showed that the intersystem crossing rate to the X spin sublevel exceeds that to the Z spin sublevel by a factor of ≈ 40. Consequently, these combined data show that the total intersystem crossing yield must be $\approx 10\%$, which is significantly higher than estimated previously.[11]

When considering the calculations given in this section, a limitation of the model has to be mentioned which can effect the accuracy of the results. We assumed in the model a square wave pulse profile in time. The pulse shape in our experiments, however, is not known, but is definitely not a square wave. Therefore, the integration in Eq. (17) is not entirely correct in this case. The inaccuracy in determining pulse shape and width also affects the calculated value for the pulse area. Furthermore, the condition $\Delta\tau \ll 1$ is not met, indicating that only part of the inhomogeneous width contributes to the echo phenomenon. Considering these points, we estimate that the inaccuracy in γ and β can be as high as a factor of 2. Note, however, that this does not affect the physical picture presented in this paper nor the conclusions drawn from the calculations in this section. Finally, it seems worth mentioning that there appears to be a discrepancy between our results and those of van Strien and Schmidt[10] on the decay time of the long living Z spin sublevel. We note, however, that by using their Z spin sublevel lifetime (280 μs) we would conclude that the ISC yield approaches 100%, which is unrealistic. Presently, we have no explanation for this discrepancy.

IV. CONCLUSIONS

The theory presented in this paper gives quantitative expressions for the accumulated echo intensity which depends only on the decay parameters, power density, and the oscillator strength of the transition studied. This means that information about an unknown decay parameter (e.g., the ISC) can be obtained from the (absolute) photon echo intensity, which is rather unexpected since usually only the decay of the relative intensity is considered.

Furthermore, these theoretical results are important for possible applications of the accumulated echo method to other molecular and atomic systems. Provided that a suitable bottleneck is present, the accumulated echo technique is a simple and convenient method for studying directly dephasing and relaxation phenomena on a picosecond time scale.

ACKNOWLEDGMENTS

We gratefully acknowledge the constructive criticism of the referee on the manuscript. We are further very much indebted to Dr. H. de Vries of this laboratory, for a thorough check of all the equations used in the manuscript and stimulating discussions. The investigations were supported by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for the Advancement of Pure Research (ZWO).

[1] W. H. Hesselink and D. A. Wiersma, Phys. Rev. Lett. 43, 1991 (1979).
[2] W. H. Hesselink and D. A. Wiersma, J. Chem. Phys. 73, 648 (1980).
[3] W. H. Hesselink and D. A. Wiersma, J. Chem. Phys. 74, 886 (1979).
[4] I. D. Abella, N. A. Kurnit, and S. R. Hartmann, Phys. Rev. 141, 391 (1966).
[5] S. L. McCall and E. L. Hahn, Phys. Rev. **183**, 457 (1969).
[6] See, for example. L. Allen and J. H. Eberly, *Optical Resonance and Two Level Atoms* (Wiley, New York, 1975).
[7] R. Loudon, *The Quantum Theory of Light* (Clarendon, Oxford, 1973).
[8] H. M. Gibbs and R. E. Slusher, Phys. Rev. A **6**, 2326 (1972).
[9] E. P. Ippen and C. V. Shank, Appl. Phys. Lett. **27**, 488 (1975).
[10] A. J. van Strien and J. Schmidt, Chem. Phys. Lett. **70**, 513 (1980).
[11] H. deVries and D. A. Wiersma, J. Chem. Phys. **70**, 5807 (1979).